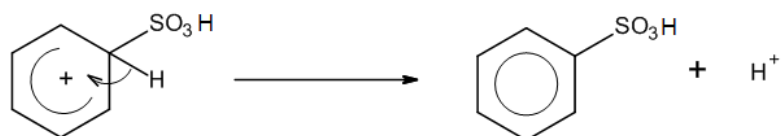
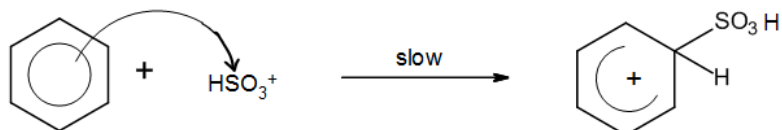
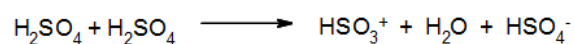
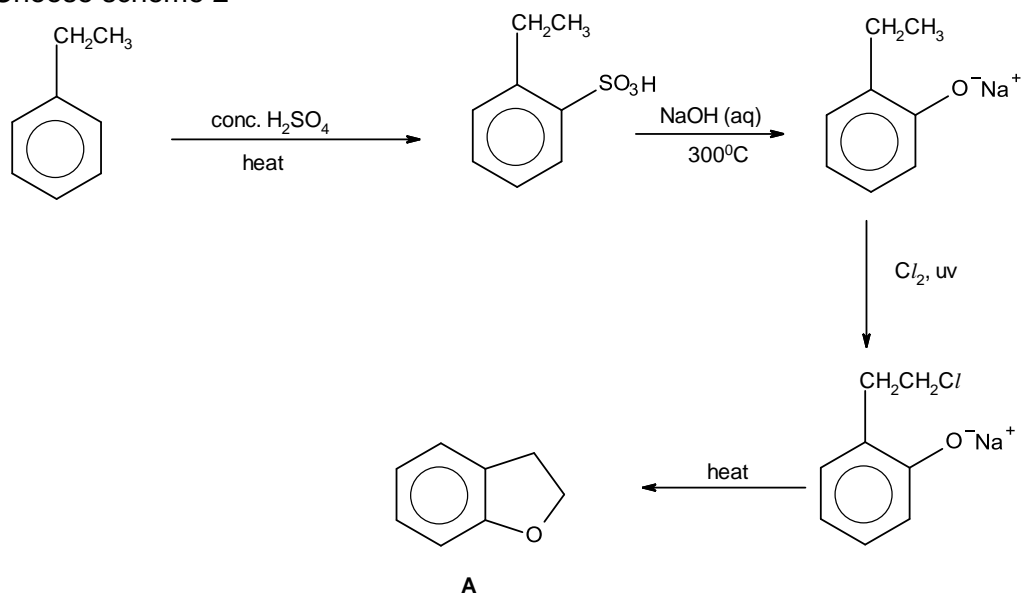


**2016 Y6 H2 Chemistry Preliminary Examination Paper 3
(Answer Scheme)**

1 (a) (i) Electrophilic substitution

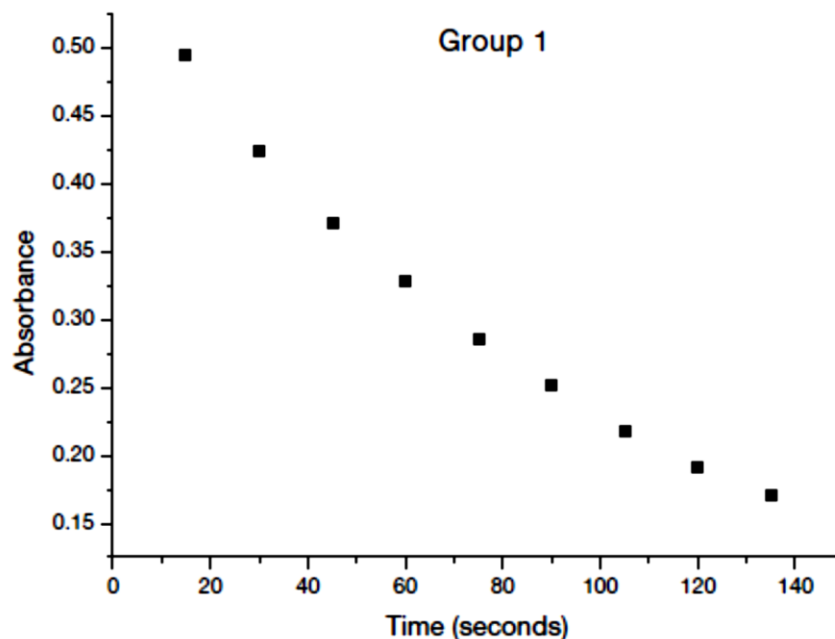


(ii) Choose scheme 2



(b) (i) To ensure that [bleach] remains almost constant throughout the reaction so that the rate can be measured with respect to Blue #1 in a pseudo-order reaction.

(ii)



From graph hand-plotted,

when absorbance decreases from 0.40 to 0.20, $t_{1/2} \approx 78$ s

when absorbance decreases from 0.50 to 0.25, $t_{1/2} \approx 76$ s

Since almost constant $t_{1/2} \approx 77$ s is observed, the order of reaction wrt to [Blue#1] is 1.

OR

Reaction is first order with respect to [Blue#1].

(iii)

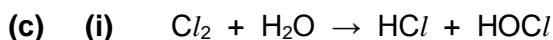
Using $t_{1/2} = \ln 2 / k$, find value of k for experiment 1.

$$k = \ln 2 / 77 = 0.00900 \text{ s}^{-1}$$

Compare experiment 1 and 3, when the volume of bleach doubles, rate constant almost doubles (i.e. $0.01498 / 0.00900 = 1.67 \approx 2$).

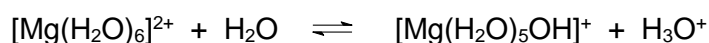
The reaction is first order with respect to [bleach].

Hence, overall order of reaction is 2.

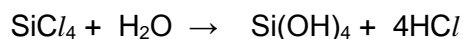


(ii) MgCl_2 is an ionic compound which ionises in water to form hydrated Mg^{2+} and Cl^- ions.

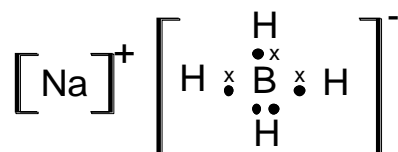
As Mg^{2+} has a high charge and small ionic radius / has a high charge density, it hydrolyses slightly in water to form a weakly acidic solution of pH 6.5



SiCl_4 is a covalent compound which hydrolyses in water to form an acidic solution of pH 2.



2(a) (i)



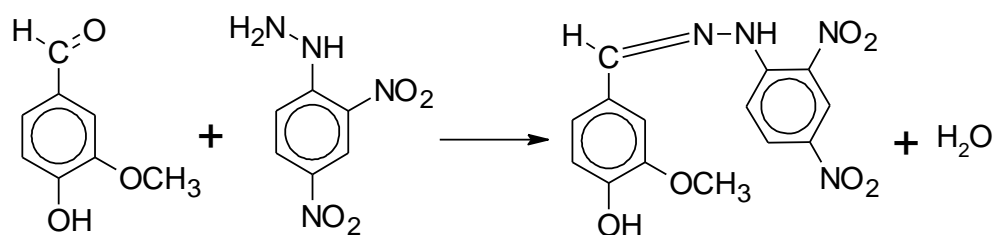
- (ii) Sodium borohydride is a milder reducing agent and hence is less reactive and will not react as violently with water present.

OR

Lithium aluminium hydride is a very strong reducing agent and hence is highly reactive and will react violently with water present.

- (iii)
 - At 360 K, vanillin is a liquid while vanillyl alcohol is a solid. There is a decrease in the degree of disorderliness, hence the entropy change of reaction at 360 K is negative.
- (iv)
 - ΔH° and ΔS° will change as temperature increases.
 - ΔG° may become more/less negative as temperature increases.
- (b) (i) The reaction is exothermic / large amounts of heat will be produced. If it was added all at once and this may cause NaBH_4 to decompose.
- (ii) $\text{NaBH}_4 + 3\text{H}_2\text{O} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_3\text{BO}_3 + 4\text{H}_2$
- (iii) Use excess NaBH_4 as it may decompose at high temperatures. Allow reactants to stir for a longer period.
- (iv) To the aliquot drawn out, add a small amount of 2,4-DNPH.

An orange precipitate will be seen if vanillin is present.

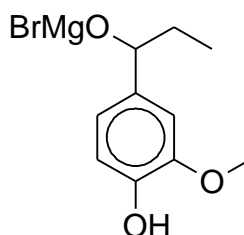


(c)	(i)	<table border="1"> <thead> <tr> <th>W</th><th>X</th><th>Y</th></tr> </thead> <tbody> <tr> <td></td><td></td><td> or </td></tr> </tbody> </table>	W	X	Y			or
W	X	Y						
		or						

Step 2: alcoholic KOH, heat under reflux
 Step 4: phenol, room temperature

- (ii)
- Vanillic acid has a higher boiling point.
 - Due to proximity of -OH and -COOH groups, 2-hydroxy-3-methoxybenzoic acid is capable of forming intramolecular hydrogen bonding, thus reduces the extent of intermolecular hydrogen bonding formed.
 - More energy is needed to overcome the more extensive intermolecular hydrogen bonds in vanillic acid.

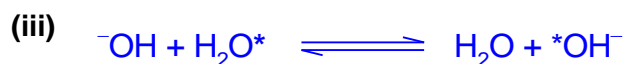
(d)



- (ii)
- Charge density: $\text{Li}^+ \left(\frac{1}{0.06} \right) \ll \text{Mg}^{2+} \left(\frac{2}{0.065} \right)$
 - Polarising power: $\text{Li}^+ \ll \text{Mg}^{2+}$ OR
 Distortion of electron cloud of NH_2^- by both cations: $\text{Li}^+ \ll \text{Mg}^{2+}$
 - Therefore LiNH_2 will have a higher decomposition temperature than $\text{Mg}(\text{NH}_2)_2$.

3 (a) (i) Nucleophilic addition

- (ii) NaOH provides the OH^- ions which is a stronger nucleophile for the nucleophilic attack on the carbonyl carbon.



The OH^- will deprotonate the ^{18}O -enriched water to form the ${}^*\text{OH}^-$. ${}^*\text{OH}^-$ then attacks the methanal via nucleophilic addition reaction.

- (iv) The carbonyl carbon in aldehyde is less sterically hindered than that in ketones, hence more easily attacked by the nucleophile.

OR

The carbonyl carbon in aldehyde is more electron deficient (δ^+) than that of ketones as ketones have an additional electron donating alkyl group.

- (b) (i) 2-hydroxyethanoic acid has a larger K_a as it is a stronger acid.



The electron-withdrawing OH group disperses the negative charge on the conjugate base of 2-hydroxyethanoic acid / 2-hydroxyethanoate ion hence stabilising the conjugate base/ 2-hydroxyethanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^+ ions, resulting in 2-hydroxyethanoic acid being a stronger acid.

OR

Intramolecular hydrogen bond can be formed in the 2-hydroxyethanoate ion between the carboxylate ion and the H of the alcohol group hence stabilising the conjugate base/ 2-hydroxyethanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^+ ions resulting in 2-hydroxyethanoic acid being a stronger acid.

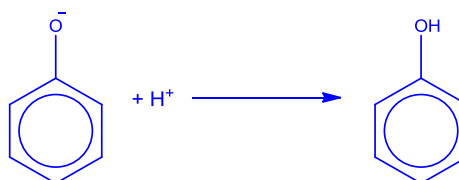
- (ii) If both indicators are used in larger amount, a larger volume of sodium hydroxide will be used to reach the end-point to deprotonate the indicators which are also weak acids.

- (iii) $X = 3.86$

X corresponds to the pH of the buffer at maximum buffering capacity.

At maximum buffer capacity, $\text{pH} = \text{p}K_a$

- (iv)



- (v) First end-point corresponds to the neutralisation of 2-hydroxyethanoic acid.

$$\text{Concentration of 2-hydroxyethanoic acid} = \left(\frac{17.20}{1000} \times 1 \right) \div \frac{20}{1000}$$

$$= 0.860 \text{ mol dm}^3$$

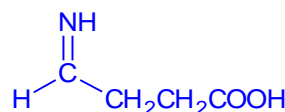
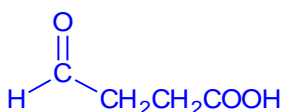
Second end-point corresponds to the neutralisation of phenol.

$$\text{Volume of NaOH used for reaction with phenol} = 26.80 - 17.20 = 9.60 \text{ cm}^3$$

$$\text{Concentration of phenol} = \left(\frac{9.60}{1000} \times 1 \right) \div \frac{20}{1000}$$

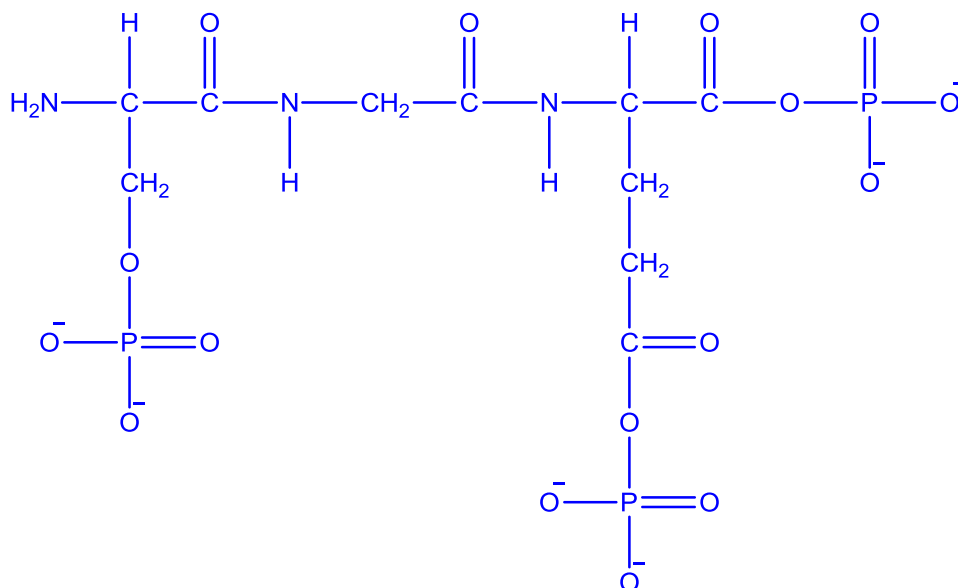
$$= 0.480 \text{ mol dm}^3$$

- (c) (i)



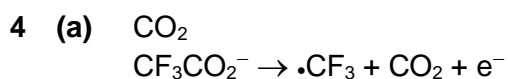
- (ii) Strecker's synthesis produces a racemic mixture and hence, do not display any optical activity while naturally occurring glutamic acid is present as one of the enantiomers and will rotate plane polarised light.

- (d) (i)

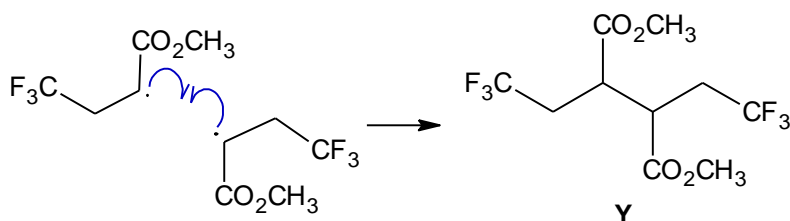
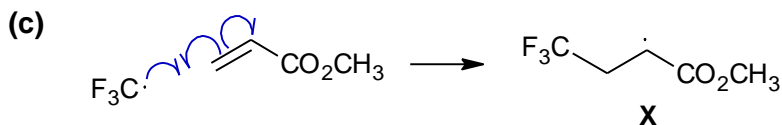


- (ii) The alpha helix is held in place due to hydrogen bonding. Hydrogen bonding occurs between the peptide $-\text{C}=\text{O}$ group of the n th amino acid and the peptide $-\text{NH}$ group of the $(n+4)$ th amino acid which is in the adjacent turn.
- (iii) Heat increases thermal vibrations of the protein molecule, disrupting van der Waals' interactions formed between uncharged R-groups in the tertiary/quaternary structure.

The hydrogen bonds between polar R groups in tertiary structure are also broken.



(b) +3



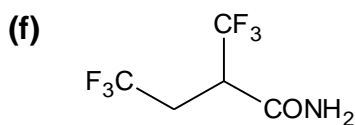
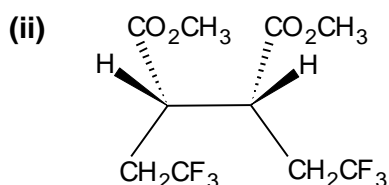
(d) (i) time = $23/20 \times 60 = 69$ s

(ii) $n(\text{Y}) = 0.401/310 = 0.0012935$ mol
 Since $2\text{e}^- \equiv 2\cdot\text{CF}_3 \equiv 2\text{X} \equiv \text{Y}$,
 $n(\text{e}^-) = 0.0025870$ mol

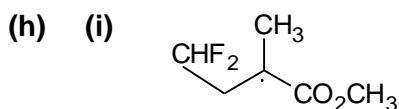
$$Q = (0.0025870)(96500) = 249.65 \text{ C}$$

$$I = 249.65/69 = 3.62 \text{ A}$$

(e) (i) 3



(g) The C–F bonds in the $-\text{CF}_3$ group are relatively strong and hence inert to chemical reactions.



(ii) The presence of the methyl group at the C atom with the unpaired electron makes it more sterically hindered. It is more difficult for two bulkier radicals to collide effectively to form the dimer.

(i) I $\text{CuL}^+ > \text{CdL}^+ > \text{NiL}^+$

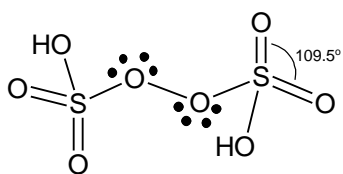
II $\log K(\text{Cu}^{2+}\text{-CH}_3\text{COO}^-) > \log K(\text{Cu}^{2+}\text{-HCOO}^-)$

From the table, the stability of the complexes is in the same order as the availability of the lone pair of electrons on the negatively charged oxygen of the carboxylate anions for dative bonding with the metal ion. Since the lone pair of electrons on the negatively charged oxygen of CH_3COO^- is more available than that of HCOO^- for dative bonding with Cu^{2+} , the $\text{Cu}^{2+}\text{-CH}_3\text{COO}^-$ complex is expected to be more stable than the $\text{Cu}^{2+}\text{-HCOO}^-$ complex.

- 5 (a)
1. Weigh the original sample first.
 2. Add aqueous sodium hydroxide in excess.
 3. Only aluminum oxide will dissolve to form a soluble complex:
 $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl}(\text{OH})_4$
 4. The mixture is then filtered.
 5. Dry the residue and re-weigh the sample again.
 6. If there is contamination, then there should be a difference in mass.

- (b) (i) The molecular formulae suggest that the structure of chlorosulfonic acid is derived from that of sulfuric acid, with $-\text{O}$ atom being replaced by $-\text{Cl}$ atom. Hence the extent of hydrogen bonding is lesser between chlorosulfonic acid molecules and hence requires less energy to overcome, giving it a lower boiling point.

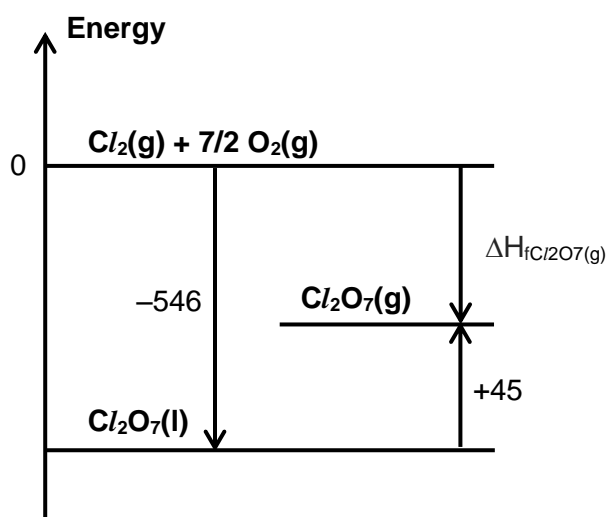
(ii)



- (c) (i) $\text{Cl}_2(\text{g}) + 7/2 \text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}_7(\text{l})$
- (ii) Bond energy of $\text{Cl}-\text{Cl} = 244 \text{ kJ mol}^{-1}$
 Bond energy of $\text{O}=\text{O} = 496 \text{ kJ mol}^{-1}$
 $-546 = 244 + 7/2(496) - [2 \times 269 + 6(\text{Cl}=\text{O})]$
 Bond energy of $\text{Cl}=\text{O} = +331 \text{ kJ mol}^{-1}$

- (iii) Vaporisation of $\text{Cl}_2\text{O}_7(\text{l})$

(iv)



By Hess' Law,
 $\Delta H_{fC/2O7(g)} = +45 + (-546)$
 $= -501 \text{ kJ mol}^{-1}$

(d)

